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MEASUREMENTS OF RESIDUAL CHLORINE LEVELS IN COOLING WATER. AMPEROMETRIC METHOD

Ronald M. Manabe

National Environmental Research Center
Corvallis, Oregon

August 1974

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This report is concerned with modification of the amperometric titration method for chlorine residuals in cooling tower blowdowns or other water systems with a high degree of metal ion content along with other dissolved and suspended solids. The addition of sodium pyrophosphate as a blanket complexing agent appears to remove successfully the heavy metals interferences contributed by Fe and Cu in the blowdown matrix.

Procedure recommendations are made to increase the efficiency of both sampling and the actual titration procedure in order to allow a residual determination in the minimum amount of time. Equipment recommendations along with a design of a biamperometric endpoint system which allows greater titration speed along with portability are described.

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MEASUREMENT OF RESIDUAL CHLORINE LEVELS IN COOLING WATER--AMPEROMETRIC METHOD

by

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Program Element 1BB392
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ABSTRACT

This report is concerned with modification of the amperometric titration method for measuring chlorine residuals in cooling tower blowdown. This modified procedure can be applied to other water systems with a concentration of metal ions similar to those found in cooling tower blowdown. The addition of sodium pyrophosphate as a complexing agent removes the interferences contributed by Fe (III) and Cu (II) in the water matrix.

Procedure recommendations are made to increase the efficiency of both sampling and the actual titration procedure in order to allow a residual determination in the minimum amount of time. Equipment recommendations along with a design of a biamperometric end point system which allows greater titration speed along with portability are described.

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CONCLUSIONS

Experimental results have shown that the analytical difficulties in the application of the amperometric technique to cooling tower blowdown can be eliminated by the addition of a pyrophosphate reagent to the currently used amperometric procedure. Copper and iron in concentrations found in typical blowdown do not interfere in the presence of pyrophosphate.

Suspensions of sediments exhibit stable end points with good recovery of incremental additions of chlorine once the initial chlorine demand of the system is satisfied.

Various synthetic blowdowns are evaluated as to stability of the end point. All of these exhibit stable end points with good recovery of the chlorine spikes once the demand constituents were satisfied. The effect of agitation when using a commercial instrument does cause an appreciable error in results if the titration is not performed rapidly. The source of the error may be due to actual flashing off the residual chlorine or enhanced photodecomposition resulting from an increase in surface area provided by the agitation.

A modified biamperometric titrator is described and evaluated. When using this titrator, results on the recovery of chlorine along with precision of the measurement are comparable to that of a commercially available instrument. The dual electrode system offers numerous advantages for field operation in that a liquid reference electrode is no longer needed. The system is battery operated eliminating the need for an AC power source. The big advantage is the rapid determination of the end point. The meter response is faster for the biamperometric method over the commercial instrument. This permits more rapid addition of titrant and easily meeting the goal of performing a titration in less than 1.5 minutes.

RECOMMENDATIONS

Further tests of the pyrophosphate system should be made on site on actual blowdown systems to check its effectiveness in the elimination of interferences due to metal ions. Feedback from other laboratories would be helpful in determining whether the pyrophosphate system would be effective in most blowdown matrixes. Due to the lack of time complete evaluation of the bioamperometric endpoint detector was not made. Further tests on its application for the analysis of total chlorine residuals should be made, perhaps by other interested laboratories. If the pyrophosphate system is not adequate in some systems, a mixture of complexation reagents should be looked into. A precipitation reagent could also be used.

INTRODUCTION

The goal of the project is the development of a simple, accurate method for the analysis of residual chlorine by the quantification or elimination of certain interferences typically present in cooling tower blowdown. Suspected interferences are turbidity, copper, iron and the chlorine reaction with phosphonates and polyesters in the water treatment chemicals used as corrosion inhibitors.

There are basically two classes of chlorine analysis, colorimetric and titrametric. The problem with colorimetric procedures is the use of comparison standards along with a spectrophotometer or color comparator. The colorimetric class of analysis requires the ability to differentiate the ways light interacts with the colored species in a sample. The physical characteristic of the blowdown water, having a high degree of turbidity and suspended solids, does not allow easy discrimination by an instrument or the human eye. The field stability of colored standards is also highly unreliable. For these reasons a titration method is a more reasonable approach in the field than a colorimetric method.

There are at present two titration methods available in Standard Methods (1) and ASTM (2). The amperometric end point technique is the Referee Method in ASTM (2). This involves the reduction of an active halogen species, either hypochlorite ion in the free residual test or liberated I_2 in the combined residual determination, by phenylarsine oxide (PAO).

$$C_6H_5AsO + HOCl + H_2O \rightarrow C_6H_5AsO(OH)_2 + HCl$$

$$C_6H_5AsO + I_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2HI$$

By lowering the pH to 4 the addition of iodide produces free I_2 in solution by oxidation of I^- by both the free hypochlorite and combined chlorine not available as chloride. The effectiveness of the phenylarsine oxide as a titrant is pH independent.

Also mentioned is a tentative procedure using ferrous ammonium sulfate as the titrant with DPD (N,N-diethyl-p-phenylene diamine sulfate) as an end point indicator. This procedure has certain features which detract from its desirability in the field application to blowdown water. One flaw is the chemical instability of the titrant which necessitates frequent standardization. The second flaw is that in extremely colored water systems with a high degree of suspended solids along with high turbidity the end point is not sharp and easily recognized. In clear water systems, however, the DPD titration technique allows differentiation among all active chlorine forms at the same pH. This is a big advantage over the amperometric method which requires a change in pH from 7 to 4 to detect free and combined chlorine residual. An abrupt change in pH can change the chemical eequilibria thus distorting the true free and combined chlorine fractions (6).

Certain weaknesses of the amperometric titration are mentioned by Nicolson (4) and Hässelbarth (5). The primary one is the flashing of chlorine out of solution or enhanced photodecomposition by the stirring action of the amperometric titrator. Another deals with the incomplete reaction of the phenylarsine oxide titrant with the chlorine residual. Hässelbarth suggests the addition of a catalytic quantity of iodide to allow the titrant to react completely. He notes that monochloramine does not increase the diffusion current between the electrodes nor does monochloramine require any titrant after the addition of KI solution.

His work, however, conflicts with the procedure in Standard Methods for the determination of monochloramine. Standard Methods suggests the addition of 0.2 ml of a 0.1N KI solution at the end point of the free residual titration to obtain a monochloramine fraction. The interpretation of the results when KI is added is at this moment in question. Since this report deals with only total residual chlorine, it is not necessary to resolve this question.

Guter and Cooper (6), in a paper evaluating various field test procedures for the determination of free chlorine residual in aqueous solutions, suggest the following improvements in the amperometric procedure:

1. Exposing the samples to as little light as possible. (VERY IMPORTANT).

2. Adding a considerable quantity (90 percent) of the titration solution before turning on the cell stirrer.

3. Completing the titration as quickly as possible.

Guter and Cooper (6) also note that the determination of free residual and combined residual on the same sample gives erratic results on the free residual determination of subsequent samples. They suggest rinsing the cell four times with distilled, chlorine demand-free water between each sample to remove all traces of iodine before another sample is run. This interference can be overcome by the use of two separate titrators: one for the free and one for the total residual chlorine fractions. Thus, taking into account the physical characteristics of cooling tower blowdown and the desirability of a fast, simple technique for the determination of chlorine residuals, the amperometric titration procedure shows the greatest promise. Reviews of alternate methods and their limitations are given in papers by Marks (7), Nicolson (4) and Palin (3).

The experimental work of the project is divided into three phases. Phase one is devoted to method familiarization. Phase two deals with an overview in which characterization of various waters as to major cations, anions and nitrogen compounds is made. Characterization allows prediction of changes in chlorine residual due to interfering reactions. Phase three involves the development of a fast, accurate procedure free of the interferences noted in cooling tower blowdown.

METHOD FAMILIARIZATION

Double distilled water as used in the Pacific Northwest Environmental Research Laboratory had a negligible chlorine demand as determined by the amperometric titrator. The water was subjected to chemical analysis weekly and the concentration of the major demand agent for free residual chlorine, ammonia, was always less than 0.001 mg/l.

The chlorine stock solutions were prepared from commercial sodium hypochlorite solutions (Clorox-5.25 percent NaOCl).

Each ml of sodium hypochlorite in bleach contained 50 mg/ml of active chlorine. A stock solution of 100 mg/l was produced by dilution of 2 ml of bleach solution to one liter with chlorine demand-free water. The dilute chlorine stock solution was standardized against thiosulfate as outlined in Standard Methods (8).

Aliquots of this stock were added to the amperometric titration vessel containing (2x) distilled water. Reagents were added as outlined in Standard Method 114B, and the titration run. The amperometric titrator used was a Wallace & Tiernan and the procedure employed is outlined in Standard Methods (9). The results are shown in Table 1.

TABLE 1

Recovery of Free Chlorine Residual (pH7)

Conc. of Chlorine Added (mg/l)	Chlorine Residual Recovered (mg/l)	Net Loss of Chlorine Residual (mg/l)
1.05	0.96	0.09
1.05	0.98	0.07
1.05	0.95	0.10
1.05	0.95	0.10
0.52	0.48	0.04
0.52	0.47	0.05
0.52	0.48	0.04
2.10	1.98	0.12
2.10	1.97	0.13

As indicated in Table 1, the free residual as determined by the amperometric procedure in the absence of iodide gives a lower value for the free residual chlorine on the order of 6-10 percent. Similar low readings were presented in the Analytical Reference Service Report Number 40 (10).

Ammonia in the form of ammonium chloride was added to known amounts of a chlorine solution to check on the recovery of free and combined fractions of the residual chlorine. Results are shown in Table 2.

The importance of the data in Table 2 is that the added step to determine both free and combined residual chlorine (1) caused consistently lower recovery of total residual chlorine. This lower reading is probably due to the flashing off of the combined chlorine residual during the free residual determination. This effect was also noted by Marks (7). Direct lowering the pH to four from the start and determining only total residual allows more complete recovery of the chlorine residual at a low pH. The loss of I_2 has been reported to be negligible (7).

The effect of varying the concentration of ammonia and looking at the free and combined residual fraction was not pursued due to the fact that the project scope was concentrated only to total chlorine residual. However, the "flashing off" effect was investigated.

TABLE 2

Recovery of Free and Combined Chlorine
in
Chlorine Demand-Free Water

mg/l Chlorine Total Added	mg/l Ammonia Nitrogen Added	mg/l Free Chlorine Residual Determined	mg/l Total Residual Chlorine Determined
2.04	0.00	1.98	--*
2.04	1.00	--*	1.98
2.04	1.00	--*	1.90
2.04	1.00	--*	1.88
2.04	1.00	--*	1.97
2.04	1.00	--*	1.90
2.04	2.00	0.74	1.80
2.04	2.00	0.78	1.88
2.04	1.00	1.18	1.74
2.04	1.00	1.20	1.83
2.04	1.00	1.26	1.60
2.04	1.00	1.28	1.84
2.04	1.00	1.26	1.81
2.04	1.00	1.26	1.83

*Determination not made

CHARACTERIZATION OF INTERFERENCES

TIME INTERFERENCE

Samples of chloramine T were used as a source of combined chlorine residual. A 10 ml aliquot of a 100 mg/l solution of chloramine T was allowed to stand in the titration vessel with stirring. See Table 3.

An assumption was made that the rate of flashing is proportional to the concentration of the chlorine in the sample vessel. This type of rate law is exponential in nature. The rate law has the form $f(t) = be^{Kt}$, where t = elapsed time before the titration is performed and b is the initial concentration of total residual chlorine present. Note at time t=0 for a residual concentration of 1.20 mg/l

$$f(t) = be^{-0} = b \qquad (1)$$

thus b = 1.20 mg/l

For t = 5 minutes, f(5) = 0.90 (from Table 3) and

$$0.90 = 1.20\ e^{+K(5)} \qquad (2)$$

Solving for K yields the following expression for the concentration as function of time.

$$f(t) = 1.20e^{-(0.058)t} \qquad (3)$$

To test the model another sample was allowed to stir for 10 minutes. Duplicate samples yielded 0.67 and 0.69 mg/l with an average value of 0.68 mg/l.

TABLE 3

Loss of Chlorine in Distilled Water
as
Function of Stirring

mg/l Chlorine	Stirring Time (min)	mg/l Chlorine Determined
1.20	0	1.22
1.20	0	1.17
1.20	5	0.92
1.20	5	0.89
1.20	10	0.67
1.20	10	0.69

Using the model to predict what the value would be and knowing starting time yielded 0.67 mg/l.

$$f(t) = 1.20e^{-(0.058)(10)} = 0.67 \qquad (4)$$

Nicolson (4) states that after 90 seconds of stirring he noted a 5 to 7 percent loss of chlorine. Applying our model at t = 1.5 minutes, a predicted loss of 8 percent is obtained, which compares quite favorably to Nicolson values. For a 30-second stirring time before the addition of titrant a 3 percent error is obtained. This experimental and theoretical treatment lends support to the improvement stated by the U.S. Army on the survey study of field test kits (6). They suggest the addition of 90 percent of the titrant before stirring action is initiated. This drops the chlorine or iodine concentration in solution to 10 percent allowing a slower rate of flashing of the active species in solution. This, however, is very difficult to do in the field if the exact end point is not known. In this case the titration should be carried out as rapidly as possible. Once experience with a given dynamic system is obtained, addition of 90 percent of the titrant should be practical.

Another time interference study was made. A chlorine residual stock solution was prepared and eight samples were poured at once into 250 ml beakers. The beakers were then stored in the dark with one sample pulled out at 5-minute intervals. See Table 4. Total chlorine residual determination was run on the samples.

From the data in Table 4, it is apparent that without stirring in the dark, the loss of chlorine residual is negligible up to at least 35 minutes for chlorine demand-free systems.

TABLE 4

Chlorine Stability in Distilled Water
in an Unstirred Sample

mg/l Chlorine Added	Storage Time (min)	mg/l Chlorine Determined
0.30	0	0.30
0.30	5	0.30
0.30	10	0.30
0.30	15	0.31
0.30	20	0.30
0.30	25	0.30
0.30	30	0.29
0.30	35	0.30

METAL ION INTERFERENCE

It was thought that some interferences to the amperometric procedure might be due to heavy metal contamination in the blowdown water. Chemical analysis of both the makeup and blowdown water for one cooling tower gave the results in Table 5. The ratio of the metal ion content in the blowdown water to that in the makeup water was approximately 10:1 -- giving 10 cycles of concentration. Metal ions contained in the blowdown in appreciable concentration are Zn, Mn, Cu, and Fe. Marks has stated that cadmium, trivalent chromium, divalent nickel and zinc in concentrations up to 1000 mg/l had no immediate effect on the amount of current flowing though the titration cell or poisoning the electrode surface (11). He has also noted that copper in high concentrations (500 mg/l) poisons the electrode. Marks also states that manganese in its higher oxidation states does not interfere if the pH is above 3.5.

Based upon the literature data and heavy metal ion content known to exist in blowdown water, two elements (Fe (III), Cu (II)) were present in sufficiently high concentrations to cause a possible interference.

These two metal ions were added to distilled water to investigate their possible interference. Solutions of copper at concentrations as low as 0.05 mg/l exhibit a poisoning effect after two titrations. The poisoning effect manifested itself by a reduction in sensitivity and instability of the current flowing through the cell. Copper produced a general drift in the meter reading as a function of time as shown in Figure 1. Copper also gave a false chlorine residual when none was present. See Table 6.

The meter deflections exhibited erratic behavior at the end point along with the deposition of a crust on the platinum electrode. Note that

TABLE 5

Chemical Analysis Of Blowdown Water

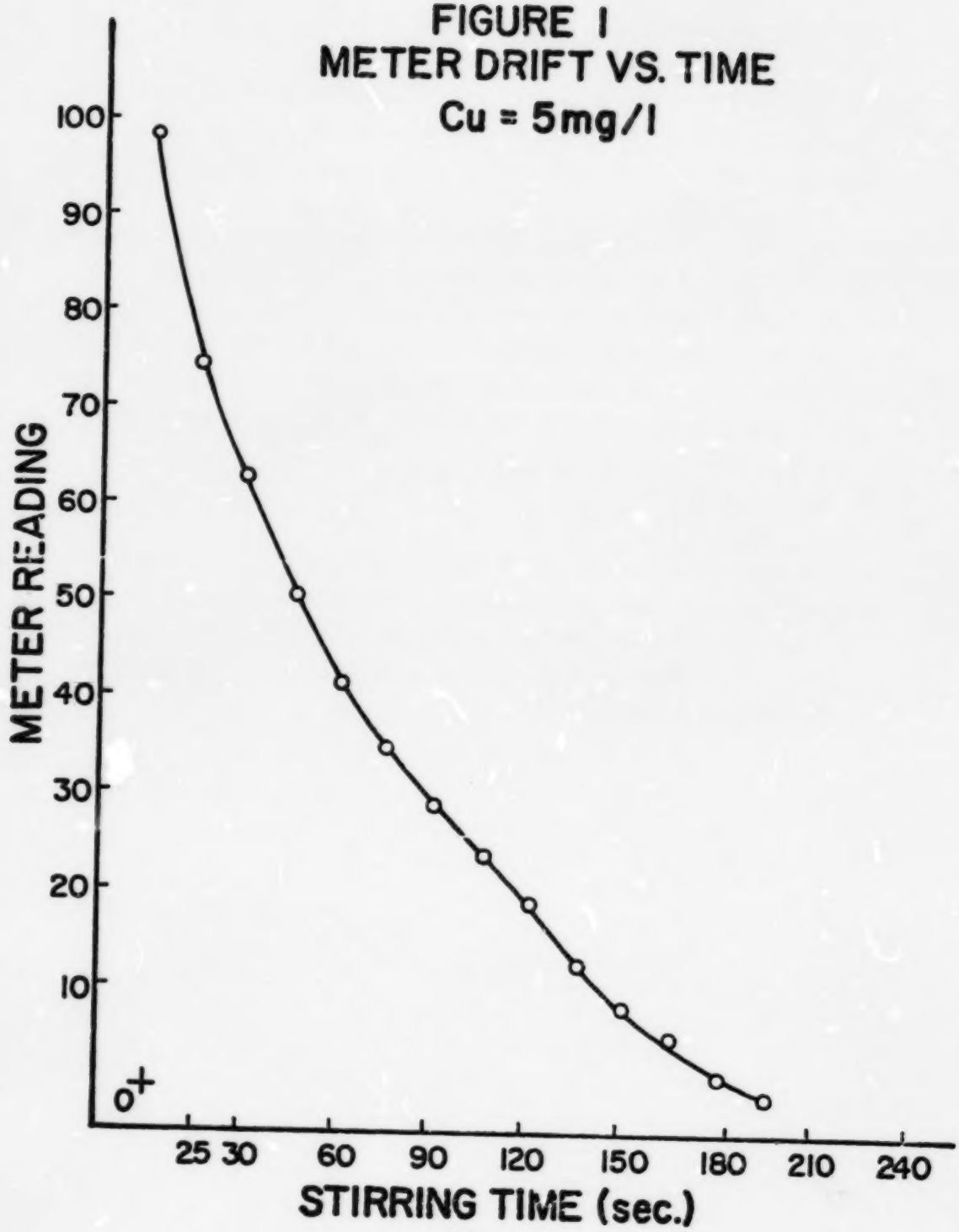
Characteristic	Cooling Tower I Makeup	Cooling Tower I Blowdown	Cooling Tower I-A Makeup	Cooling Tower I-A Blowdown	Cooling Tower II Blowdown
OIC TOC[1] (mg/l)	22.4	87.1		5	--
Kjel N[2] (mg/l)	0.38	2.4	< 0.01	0.4	--
Ammonia N (mg/l)	0.007	0.067	< 0.001	0.0025	0.0065
Nitrite N (mg/l)	0	0.025	0.003	0.0525	0.006
Nitrate N (mg/l)	0.52	6.0	0.031	0.765	0.113
Ortho P[3] (mg/l)	0.011	1.4	--	--	--
Chromium (µg/ml)	< 20	< 20	10	26000	7600
Copper (µg/ml)	20	200	5	29	11
Iron (µg/ml)	440	6000	39	39	240
Manganese (µg/ml)	10	220	4	6	1.2
Lead (µg/ml)	--	--	< 10	14	240
Zinc (µg/ml)	--	--	68	40	1200

1 Total organic carbon using Oceanography International Corp. instrument

2 Organic + ammonia nitrogen

3 Phosphorus as PO_4^{3-}

FIGURE 1
METER DRIFT VS. TIME
Cu = 5mg/l



for a residual chlorine level of 1 mg/l one series gave low results and another high results. A cumulative effect was noted in which the drift increased with each determination.

Iron in concentrations of 5 mg/l causes a similar loss in sensitivity; however, no cumulative effect was seen as in the case of copper. Low recoveries of chlorine were also obtained (approximately 85 percent).

It was concluded that copper and iron did interfere with the chlorine residual test. Other metal ions present may also interfere. To eliminate these interferences a suitable complexing agent was sought which would form a complexation product that was inert under the chemical conditions of the amperometric determination. Complexing agents tried were sodium citrate, NTA, sodium oxalate and sodium pyrophosphate.

Sodium Citrate

A 20 percent solution of sodium citrate was prepared as a stock solution. Aliquots of this stock solution were added to the titration vessel. Addition of citrate to a 5 mg/l copper solution stabilized the drifting problem. Table 7 shows a data summary of behavior of copper on the residual chlorine test.

TABLE 6

Effect of Cu (II) on Recovery
of Chlorine Residual

Cl Conc. mg/l	Cu Conc. mg/l	Residual Chlorine mg/l
0	0.05	0.01
0	0.10	0.05
0	0.15	0.04
0.98	0.05	0.96
0.98	0.05	1.00
0.98	0.10	0.88
0.98	0.10	1.07
0.98	0.15	0.99
0.98	0.15	1.05

TABLE 7

Effect of Citrate on Copper Interference

Cl Conc. mg/l	Copper Conc. mg/l	Conc. of Citrate grams/liter	Residual Cl mg/l
1 mg/l	0	0	0.99
1 mg/l	5	10	0.99

Iron in a concentration of 5 mg/l gave low recoveries of residual chlorine. See Table 8.

Iron (Fe) does not seem to form a stable complex sufficient to prevent interference. The citrate used with the iron and copper solution produced an incrustation on the platinum electrodes and this was viewed as undesirable.

NTA

The chlorine demand of NTA (nitrilo triacetate acid sodium salt) was checked by the addition of 1 gram of NTA to the titration vessel which contained a chlorine residual of 0.97 mg/l. NTA exhibited a chlorine demand of 0.06 mg/l. Addition of 5 mg/l copper and 25 mg/l iron yielded the same chlorine demand of 0.06 mg/l.

Sodium Oxalate

Sodium oxalate exhibited the same type of behavior as NTA. A 1 gram sample added to a 1 mg/l solution yielded a chlorine demand of 0.06 mg/l.

Sodium Pyrophosphate

Sodium pyrophosphate was used by Mizuno (12) to mask ferric iron in the determination of ferrous iron. Since a significant concentration of iron is present in cooling water blowdown, sodium pyrophosphate should be successful in eliminating the effects of iron on the residual chlorine determination.

A 1 gram sample of sodium pyrophosphate was added to the titration vessel. For a 1 mg/l chlorine spike all of the chlorine was recovered. Addition of copper (5 mg/l) and iron (25 mg/l) gave an average chlorine residual of 0.98 mg/l or a 2 percent lower value. This, however, is better than any of the previous complexing agents.

The pyrophosphate chelating system gave good stable end points with no drift. Meter sensitivity was down slightly but tolerable due to the lack of drift. To quantify the amount of pyrophosphate to effectively complex interfering ions a 10 percent stock solution of $Na_4 P_2O_7 \cdot 10H_2O$ was prepared as stated in the appendix; 1.4 ml was added to the titration vessel. This quantity was found to give stable end points for copper solutions up to 0.5 mg/l. This quantity of pyrophosphate was sufficient to complex 10 mg/l of iron by allowing a stable end point. A composite solution of 0.5 mg/l Cu (II) and 10 mg/l Fe (III) with 1.4 ml of pyrophosphate gave a slight drift in the end point. A 2 ml portion of pyrophosphate however, stabilized the end point. The pyrophosphate system gave no positive chlorine residual analysis in the presence of copper. The platinum electrodes remained shiny and clean.

EFFECT OF TURBIDITY

Varying amounts of turbidity were simulated by Kaolin suspensions in varying concentration. Two mls of a 0.10 mg/ml chlorine stock solution was added to the titration vessel containing 200 ml of the Kaolin suspension. The Kaolin suspension was prepared by adding 1 g of Kaolin to one liter of water and performing appropriate dilutions of this stock. Two milliliters of sodium pyrophosphate were added to the titration vessel. See Table 9.

Good recovery of the residual was obtained in Kaolin concentrations up to 500 mg/l. The effects of other solid and colloidal suspensions were examined. Two samples tested were Corvallis clay from the vicinity of the Oak Creek bank near 35th street in Corvallis and dried bottom sediment from Cline's Pond. Both sediments were sieved through 120 mesh screens to separate the fine particles for suspension. Each sample exhibited an initial chlorine demand, i.e., total recovery of the chlorine spike was not achieved. Additional spikes of chlorine were made on the system and good recovery was achieved. See Table 10.

TABLE 8

Effect of Citrate on Iron Interference
In Determination of Chlorine Residual

Cl Conc. mg/l	Fe Conc. mg/l	Conc. of Citrate grams/liter	Residual Cl mg/l
1	0	0	0.99
1	0	5	0.98
1	5	5	0.85
1	5	40	0.95

TABLE 9

Recovery of Cl in Presence of Kaolin

mg/l Kaolin	JTU	Cl Residual (mg/l)
0		0.96
25	(25)	0.96
100	(86)	0.96
500		0.94

WATER TREATMENT

A 100 mg/l solution of a phosphonate-type water treatment chemical was prepared. Solutions with no chlorine added gave no positive indication of a chlorine residual. Solutions of the water treatment chemical were spiked with known amounts of chlorine. Chlorine residuals were immediately run. The solutions were allowed to stand with a chlorine residual run at varying intervals. A data summary appears in Table 11.

From the data it is evident that the water treatment chemical does exhibit a chlorine demand. Additional spikes of chlorine to these samples allowed recovery of greater than 90 percent.

TABLE 10

Recovery of Cl Spikes on Cline's Pond Sediment
And Corvallis Clay

Sample	Recovery of Cl Spikes Spike #1 Initial mg/l	Spike #2 mg/l	Spike #3 mg/l
Cline's Pond Sediment	0.70	0.97	0.97
(100 mg/l)	0.10*	0.47*	0.48*
Corvallis Clay	0.57	0.95	0.97
(500 mg/l)			

Chlorine spikes = 0.98 mg/l
*Chlorine spikes = 0.49 mg/l

TABLE 11

Recovery of Chlorine Additions in the Presence
of a Water Treatment Chemical as a Function of Time

Contact time (hours)	Solution #1 (mg/l) Cl	Solution #2 (mg/l) Cl	Solution #3 (mg/l) Cl
0	0.66	2.18	4.09
5	0.59	0.89	3.33
69	0.38	0.00	1.46

Initial Cl Concentrations	#1	#2	#3
	1.01	2.52	5.04

PRECISION

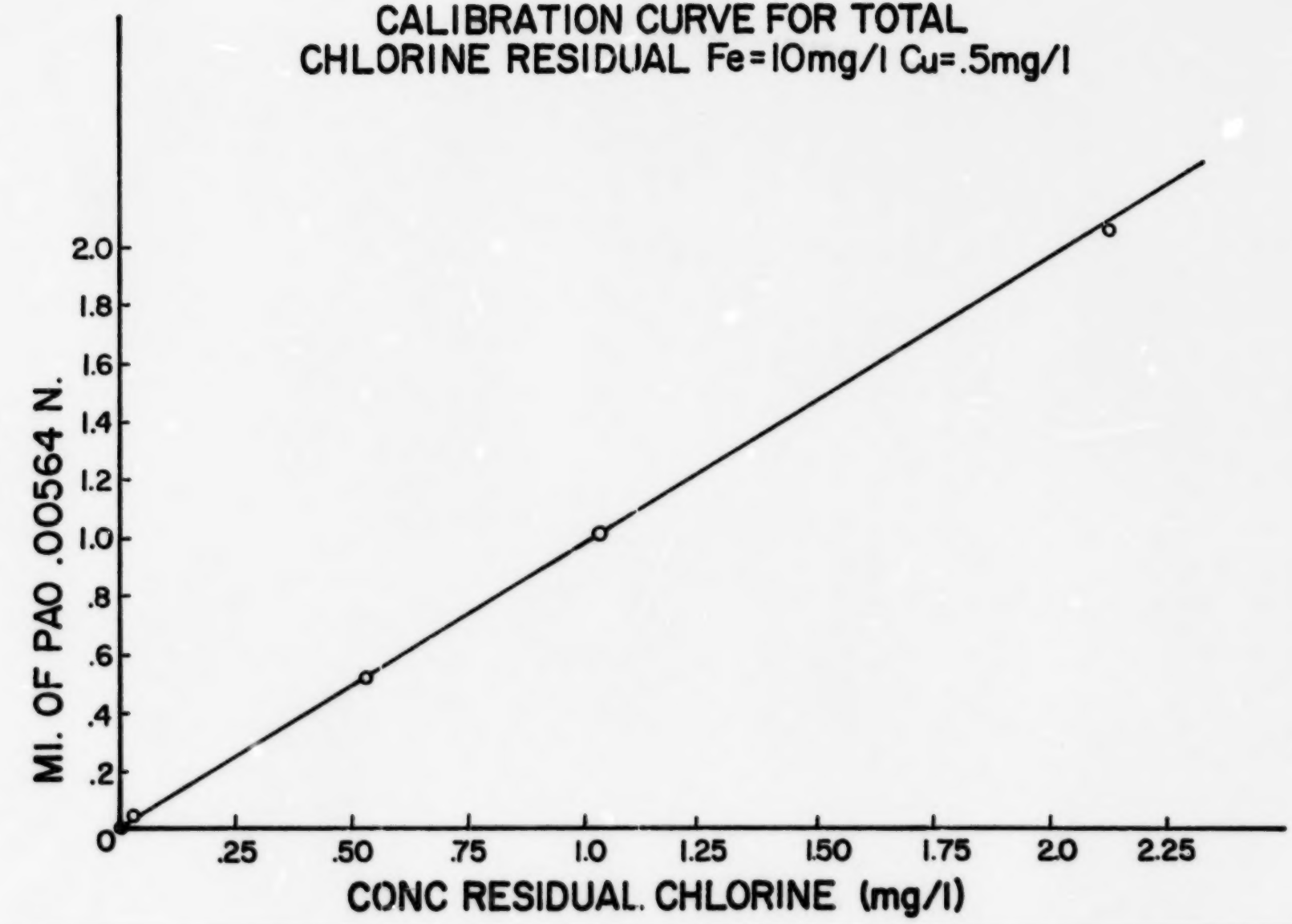
Twelve replicate runs using the procedure outlined in the appendix using the Wallace & Tiernan Titrator, were made on each concentration of residual chlorine. An average value of the chlorine residual along with the standard deviation and relative standard deviation appear in Table 12. A calibration curve was plotted for the average values of Table 12. See Figure 2. A least squares analysis was run with a correlation coefficient of 0.9999.

TABLE 12

Precision of Titration

Cl spike mg/l	Average mg/l	Standard deviation mg/l	Relative Standard deviation (%)
0.053	0.047	0.0039	8.3
0.53	0.52	0.009	1.7
1.06	1.02	0.008	0.7
2.12	2.05	0.0263	1.28

FIGURE 2
CALIBRATION CURVE FOR TOTAL
CHLORINE RESIDUAL Fe=10mg/l Cu=.5mg/l



RECOVERY RATE OF CHLORINE IN SYNTHETIC AND NATURAL BLOWDOWN

Synthetic blowdown water was prepared by slow evaporation of natural waters on a hot plate. Solutions were allowed to evaporate to an eighth of their original volume. This allows an 8-cycle concentration of cations and anions along with organic compounds. Samples chosen for synthetic blowdown were from the Buffalo River, Cuyahoga River and Cline's Pond. Chemical analysis of these sources is shown in Table 13. All samples were spiked with a chlorine stock solution to a residual chlorine level of 5 mg/l and were allowed to stand overnight to satisfy any long-term chlorine demand. A residual chlorine analysis was run on each sample. Approximately 0.5 mg/l was added to another aliquot of the natural samples and an additional residual chlorine analysis was run. The data are presented in Table 14. The last two entries to Table 14 are actual blowdown systems.

Cooling Tower I blowdown in the presence of pyrophosphate allowed a stable end point to be obtained with no positive indication of chlorine when none was present.

TABLE 13

Chemical Analysis of Natural Water Samples

Characteristic	Cline's Pond	Cuyahoga River	Buffalo River
OIC TOC (mg/l)	5	10	
Ammonia N (mg/l)	0.018		
Nitrite N (mg/l)	0.014		
Nitrate N (mg/l)	0.79		
Chromium (µg/l)	5	10	6
Copper (µg/l)	26	14	43
Iron (µg/l)	2100	900	1300
Lead (µg/l)	20	25	31
Manganese (µg/l)	33	210	58
Zinc (µg/l)	16		

TABLE 14

Recovery of Chlorine Spikes on Blowdown

Source of Sample	Total Residual Chlorine mg/l *	Chlorine Addition mg/l	Chlorine Residual After Spike mg/l	Recovery of Addition mg/l
Buffalo River	1.15	0.49	1.60	0.45
Cline's Pond	2.05	0.52	2.55	0.50
Cuyahoga River	1.12	0.52	1.61	0.49
Cooling Tower I	1.60	0.49	2.08	0.48
Cooling Tower II	1.22	0.51	1.71	0.49

*After satisfaction of initial demand and overnight standing.

BIAMPEROMETRIC END POINT

An alternate amperometric titrator was sought which might be more field adaptable. Marrow (13) described a dual, polarizable electrode (D.P.E.) method for the determination of the end point. Many advantages have been cited for this method. The first is simplicity of the electrode configuration. The electrode consists of two platinum sheets mounted in plastic, see Figure 3. This arrangement eliminates the need for maintenance of a reference electrode. The power supply for a D.P.E. method is much simpler in that an opposition voltage need not be applied to the electrodes to get the end point on scale as required by a single polarizable electrode. For a D.P.E., the end point of a reversible electrochemical system titrated with an irreversible titrant will cause the end point to occur close to zero microamps (14).

EQUIPMENT

A dual platinum electrode system similar to that described by Marrow (13) was constructed. See Figure 3.

The dual polarizable electrode system was designed in the shape of a probe for simplicity. The stirring system used was a La Pine "Porta Stirrer." This magnetic stirrer has a rechargable battery pack allowing portable operation.

The schematic diagram of the control unit appears in Figure 4. The value of the shunt resistor R is chosen such that the 10 μamp meter scale now reads 100 μamps full-scale.

The shunt system is always in the circuit unless the push button switch is physically depressed. Removal of the shunt allows full meter sen-

FIGURE 3
CHLORINE PROBE (DPE)

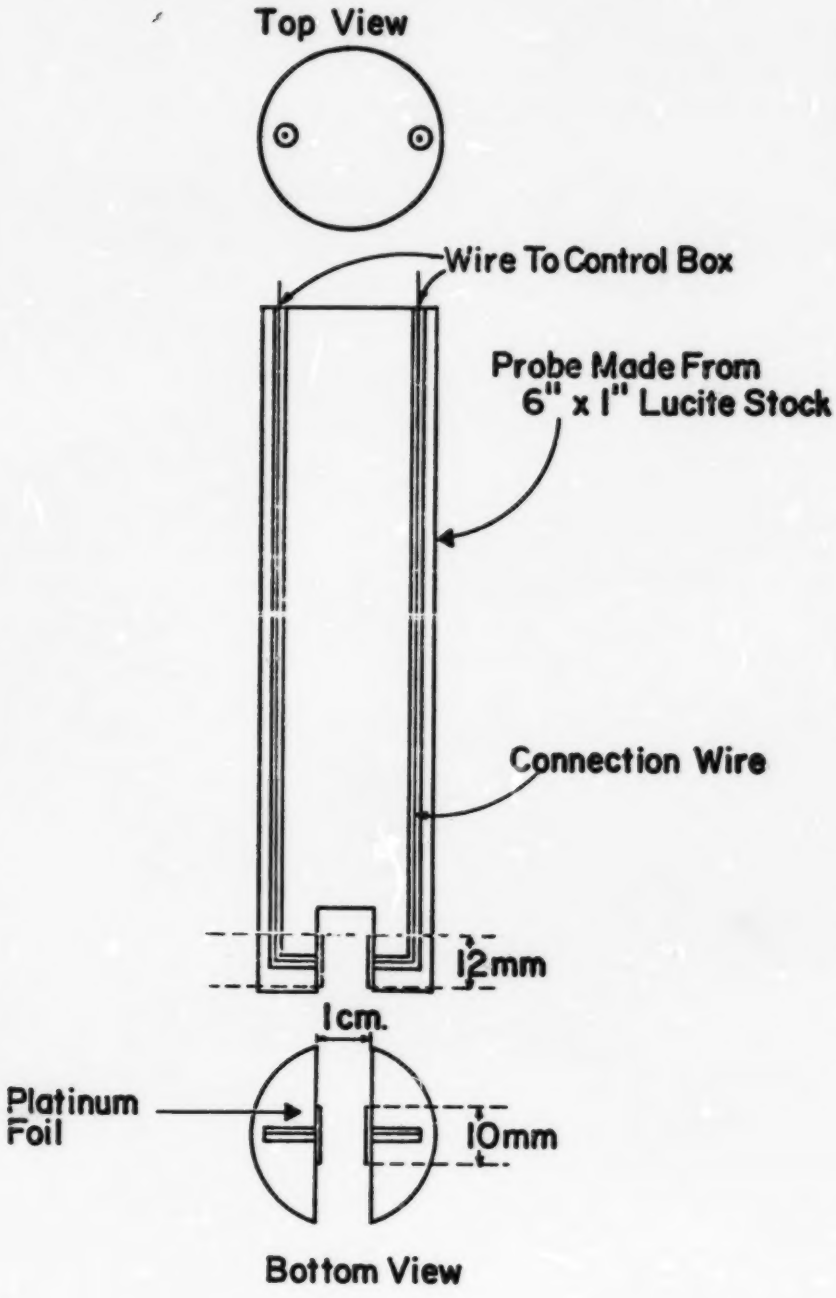
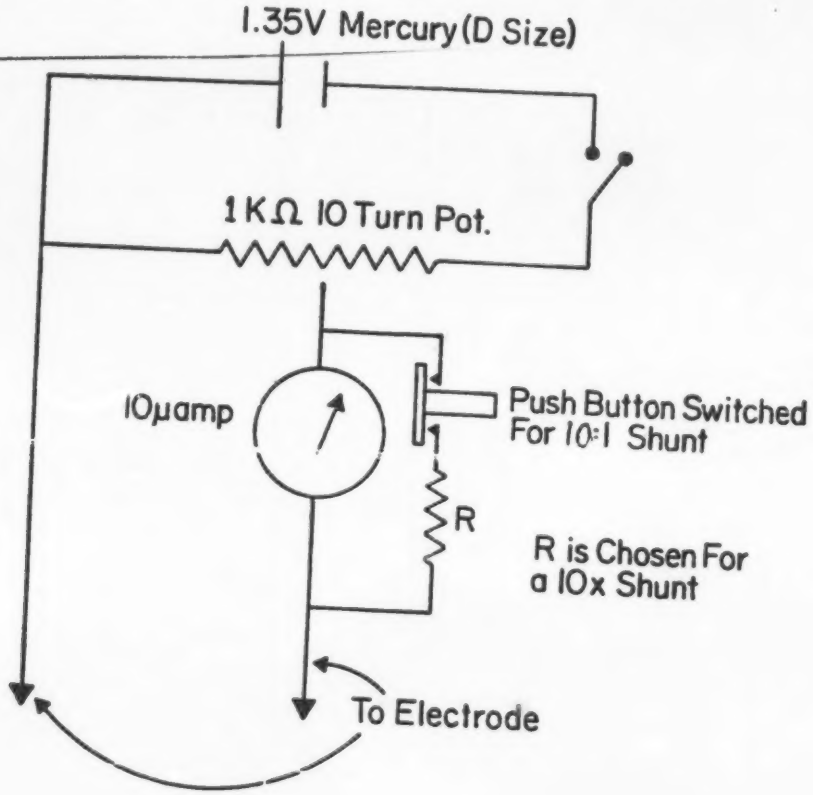


FIGURE 4
SCHEMATIC DIAGRAM OF DPE CONTROL BOX



sitivity which permits a more precise detection of the end point. Extreme care must be exercised to insure that the currents are less than 10 μamps before the shunt is bypassed or meter damage will occur.

Thus, knowing that the end point will occur at zero current, rapid addition of the titrant until the vicinity of the end point is possible, speeding up the titration procedure. The stirring mechanism for the titrator causes less vigorous agitation than that of the Wallace & Tiernan titrator minimizing the flashing problem. The stirrer can be of any configuration and may be battery operated to be field adaptable along with a battery power supply of the D.P.E.

EFFECT OF COPPER AND IRON ON D.P.E. METHOD

The effect of copper and iron in concentration analogous to those found in cooling tower blowdown was studied. The interference studied was the effect of varying the potential between the dual indicator electrodes and measuring the background currents. Plots of the relationship of background currents vs applied voltage appear in Figure 5 and Figure 6. The iron concentration was 10 mg/l and copper concentration was 0.5 mg/l. The pH was 4.

For the iron interference plot note that at applied voltages of less than 200 mv the pyrophosphate system caused a reduction in the background current to the blank level. At higher voltages the pyrophosphate system greatly reduced the background currents.

For the copper plots the effect of copper upon the background current is nil up to about 300 mv. Beyond this the pyrophosphate system reduces the background currents of copper although not as dramatic as the iron curves. Note that as long as the applied voltage is kept less than 200 mv background contribution is nil. This is an indication that these heavy metals are electrochemically inactive at these potentials.

FIGURE 5
BACKGROUND CURRENT VS APPLIED VOLTAGE
IRON INTERFERENCE STUDY

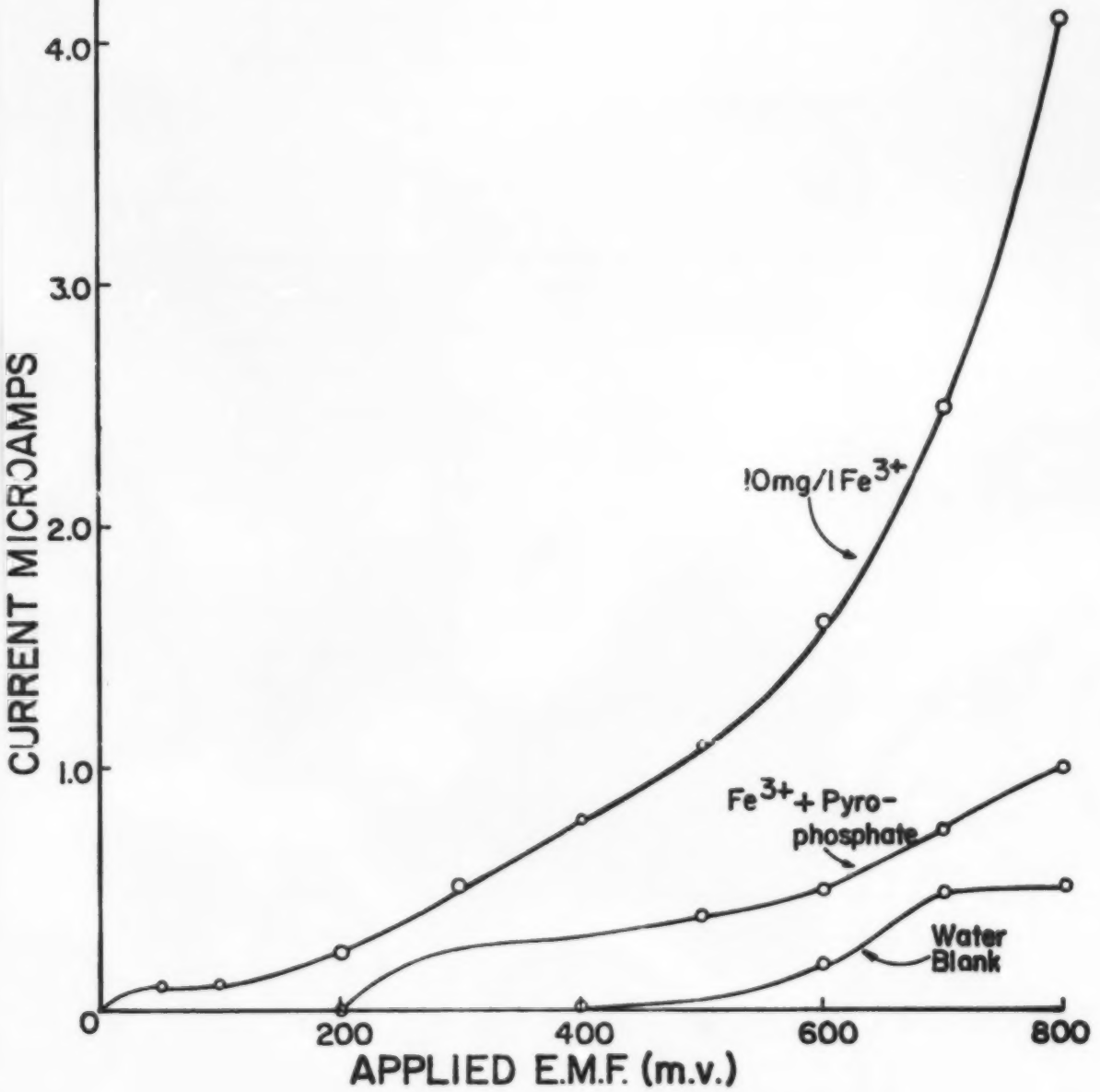
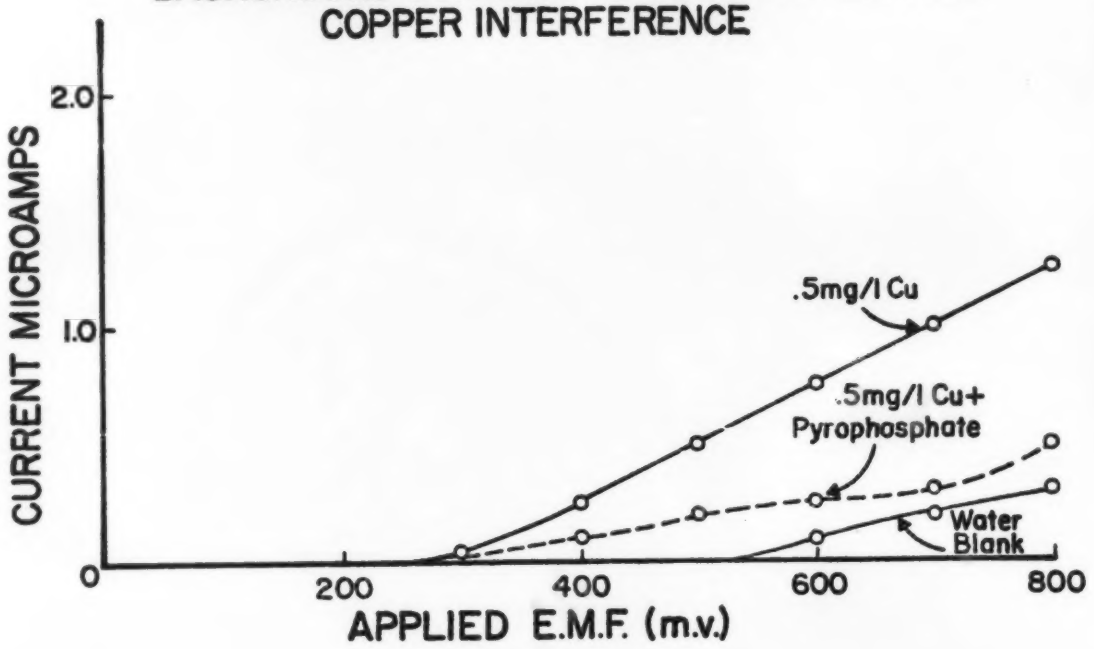


FIGURE 6
BACKGROUND CURRENT VS APPLIED VOLTAGE
COPPER INTERFERENCE



For the determination of the end point in a total chlorine residual analysis an applied voltage of 150 mv is recommended.

The presence of copper and iron did not exhibit the drifting problems noted for the Wallace & Tiernan titrator. The meter readings at high currents (7.5 μamps) showed some instability. This is probably due to nonconstant stirring. At the end point, however, the meter readings are very stable.

The recovery rate for both forms of the amperometric end point are the same and the precision comparable for total residual chlorine. The biamperometric technique offers an advantage by allowing the end point to be reached much faster.

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APPENDIX

AMPEROMETRIC TITRATION PROCEDURE

INSTRUMENTATION

The titrator employed in this report was the Wallace & Tiernan Series A-790 amperometric titrator. The buret furnished with the unit was substituted with a 5 ml autofilling microburet with calibration marks down to .01 ml. The flow of titrant was transported to the titrator through appropriate tygon tubing and tubing adaptors.

Standard Methods recommends that the volume of titrant used be less than 2 ml. For determining chlorine residuals in cooling tower blowdown within 3 minutes, a larger addition must be tolerated, hence, the use of a 5 ml buret. If chlorine residuals of greater than 5 mg/l are anticipated, a smaller sample size should be used, i.e., 100 ml instead of 200 ml. If one desires ease of titration of extremely low residuals, < .2 mg/l, dilution of the titrant would allow greater refinement of the equivalence of titrant added to the system. A separate buret system would be needed to not contaminate the stock (PAO) solution buret (0.00564N). Appropriate concentration factors must be applied to the buret readings to correlate the results to mg/l residual chlorine.

To facilitate rapid addition of these reagents of the sample vessel, syringes or autopipets are recommended. For measuring out the 200 ml samples a graduated cylinder sawed off at the 200 ml calibration mark makes rapid sample measurement easy. A small lip should be fashioned to eliminate possible spills when transferring samples to the titration vessels. A 200 ml aliquot of sample is automatically measured by dipping the cylinder into the water sample, thus filling the cylinder to overflowing.

The contents of the cylinder are carefully poured into the titration vessel without spilling. Between runs, the titration vessel should be rinsed with chlorine-free water. The sample vessel need not be dried however, since the graduated cylinder contains the active chlorine residual. All that is important is that a consistent amount of sample water is added to the vessel. Dilution by water adhering to the walls has no effect.

The titration vessel supplied with the Wallace & Tiernan titrator should be adequate--provided that a differentiation of free and combined residual is not made on the same sample. If the titrant volume is kept low, sample overflow should not be a problem.

A suitable pH meter is required to check the buffering capacity of the water sample and to check the proper amount of buffering agent required to bring the sample plus reagents to the appropriate pH.

REAGENTS

All reagents were prepared as in Standard Methods 114.B, 13th (1) edition.

The standard phenylarsine oxide was purchased from Wallace & Tiernan.

Sodium Pyrophosphate

Dissolve 100 grams of sodium pyrophosphate $Na_4 P_2O_7 \cdot 10H_2O$ in 1 liter of water heated to 50°C. Place mixture on a mechanical stirring device to bring the salt into solution. Allow the solution to cool. Add 85 percent phosphoric acid to the solution until a pH of 6 is obtained. For total residual chlorine analysis a low pH of the pyrophosphate chelate is desirable as not to overwhelm the pH4 buffer system.

TITRATION

1. Preliminary Work.

The electrode surface should be sensitized to iodine in the following procedure:

a. Fill the titration vessel with distilled water.

b. Add 1 ml of 5% KI., 1 ml pH4 Buffer.

c. Add sufficient hypochlorite to cause a yellow to yellow-brown coloring of the solution. Place vessel on titrator and allow to stir for 10 minutes.

d. After the time limit direct a stream of distilled water from a polyethylene wash bottle around the electrode to remove as much iodine as possible.

e. Fill titration vessel with distilled water and place on titrator and add with stirring .5 ml of titrant. This will remove any traces of I_2 present.

f. Remove titration vessel and rinse electrodes thoroughly by directing a stream of distilled water around the electrode. The titration vessel containing the sample can be used as a catch for the rinse water.

While the titrator is stirring in the sensitizing step a 200 ml sample of water can be obtained with the specially prepared graduated cylinder as noted in the equipment section. The purpose of this sample is to

determine the amount of buffering needed to drop the pH to 4. To the water sample add 1 ml KI, 2 ml of the 10% pyrophosphate solution. Place pH probe into sample and add increments of pH4 buffer until pH is in the range of 4 to 4.2. Add approximately 0.25 ml in excess to compensate for variations in the buffering capacity of the natural water. Two mls of a 10 percent pyrophosphate solution should be sufficient for 10 mg/l iron and .5 mg/l copper. If metal ions are significantly higher or lower, adjustment of the amount of pyrophosphate reagent should be made. A criterion for the proper amount of pyrophosphate is the stability of the end point (No drift).

If the meter deflections become erratic, this is due to salt build-up around the electrode sockets. To cure this, the electrode and the front faceplate must be removed and the salt scrapped away. A stream of distilled water can be directed at the socket holes to remove the remaining salt. The entire socket area should then be wiped dry to prevent any possible leakage currents to flow.

2. Titration Procedure.

During the actual titration run, all steps should be performed with both speed and good laboratory technique. All reagent syringes should be calibrated to deliver the proper amount of reagents. Practice with the sampling graduate should be done such that sampling is rapid and without spills. Past experience with the system in question would aid in the prediction of the amount of titrant required to reach 90 percent of the end point to eliminate loss due to agitation. Sunlight should be kept to a minimum and the titration done in subdued light.

Syringes, calibrated for proper delivery of appropriate reagents, should be placed into the opened bottles to act as lids. The potassium iodide solution should be stored in a brown bottle. Fresh KI should always be

used. If any trace of coloration is present, the solution should be discarded. (If there is any question about the KI, a titration should be performed on distilled water to which the proper amount of KI was added. If a positive indication is noted, fresh KI should be substituted.)

The actual titration procedure is similar to that in Standard Methods. (9, 10) Modification to the procedure involves the preparation and use of an additional reagent and addition of a large increment of titrant before the agitation starts. The procedure is as follows:

a. Obtain a 200 ml sample in the precalibrated graduated cylinder and pour without spilling into the titration vessel rinsed with distilled water.

b. Using the precalibrated syringes add proper amounts of KI, pH4 buffer and pyrophosphate solution. One ml of KI solution is sufficient.

c. Place titration vessel on the amperometric titrator and, if feasible, add approximately 90 percent of the final titrant volume. Start stirring action.

d. Continue the addition of titrant until the needle no longer deflects left. After the first titration the scale sensitivity control should be adjusted until the meter reads approximately 20. For subsequent titrations the end point should appear approximately at the same reading. Early in the titration the meter will be off scale. Rapid additions of the titrant can be made until the meter reads on scale.

e. Read the buret for the concentration of the chlorine residual.

BIAMPEROMETRIC TITRATION

The equipment required is a biamperometric probe, control box and magnetic stirring device. These pieces of equipment are described in the main body of this report.

Experimental Procedure Biamperometric End Point

a. The sample is obtained in the same manner as in the previous procedure. The sample vessel, in this case is a 400 ml beaker. (Electrodes need not be sensitized to iodine.)

b. The necessary reagents are added as described earlier.

c. A magnetic stirring bar is added to the beaker and the beaker placed on the magnetic stirring device.

d. The power is turned on the control box. This can remain on until the end of the sampling period.

e. The electrode probe is lowered into the solution and the stirring action started.

f. Addition of titrant is done rapidly until the scale reads less than 10 μamps. At this point the X10 button is depressed and titrant added rapidly until the meter reads close to 0 microamps. Titrant is added in small increments until the meter no longer deflects left. The last increment is then subtracted.